# Elucidation of mechanisms in manganese and iron based oxidation catalysis

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# Chapter 5

## Elucidation of the mechanism of manganese catalysed oxidation of alkenes in aqueous media at high pH

The oxidation of substrates, such as water soluble alkenes, with $H_2O_2$ with the catalyst $[Mn(IV,IV)_2(\mu\text{-}O)_3(tmtacn)_2]^{2+}$ (**1**) is studies in this chapter with the goal of elucidating the role of both 'free' Mn(II) ions and carbonate as a buffer. The chapter focuses on the effect of buffers, concentration and sequestrant on catalytic activity. The main finding is that mechanistic studies must recognize the possibility of concurrent catalytic processes being involved and consideration of the effect this has on results gained with variation in conditions and with probes is shown to be essential.

## 5.1 Introduction

The selective oxidation of organic compounds is as central to synthetic chemistry as to industrial chemical processes.[1,2] Terminal oxidants of choice are $O_2$ and $H_2O_2$, primarily due to the minimal chemical impact they and their by-products have on the environment and above all there atom and economic efficiency. The direct use of $O_2$ and $H_2O_2$, although thermodynamically favourable is kinetically impeded and hence catalysts are central to their application. Over recent decades, intensive efforts have been directed toward the discovery and development of transition metal based catalysts for the activation of $H_2O_2$, not least for dihydroxylation and/or epoxidation of olefins and oxidation of other functional groups.[3] Among the many first row transition metal catalysts reported to date, manganese complexes bearing ligands based on the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) such as **1** (Figure 1) have attracted considerable attention both for their solid state and magnetic properties and as models for bioinorganic systems.[4] In the mid-1990s, the catalytic activity of the complex $[Mn_2^{IV,IV}(\mu\text{-}O)_3(tmtacn)_2](PF_6)_2$ (**1**) was discovered in oxidation and bleaching process by Hage et al.[4b] The application of manganese complexes of tacn in a wide range of oxidative functional group transformations in organic solvents was reviewed recently by Saisaha et al.[5] and by Watkinson et al.[6]

Although the solid state and magnetic properties of these complexes have been examined in detail,[4a] the speciation of these complexes in solution and especially in water has received much less attention.[7] Recent mechanistic studies into manganese catalyzed oxidation catalysis in particular speciation analysis in non-aqueous media, have shown the key role of the formation of μ-carboxylato bridged ($[Mn(III,III)_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2(tmtacn)_2]^{2+}$) complexes (e.g., **2**) formation in the case of **1**, which determines activity and selectivity in the oxidation of alkenes.[8] It was proposed based on ESI-MS experiments and $^{18}O$-labeling studies that the dinuclear bis(carboxylato) bridged $Mn(III,III)_2(OH)(OOH)$ species is a key intermediate in the formation of epoxide or *cis*-diol products.[8] In chapter 4, the conversion of **1** to $[Mn(III,III)_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2(tmtacn)_2]^{2+}$ was studied in detail using a combination of UV/Vis absorption, electron paramagnetic resonance (EPR), Raman and resonance Raman (rR) spectroscopy. We proposed that the conversion proceeds by an autocatalytic mechanism and that the species that is responsible for the oxidation of the organic substrates also catalyzes $H_2O_2$ decomposition, and the former process is competitive.[9] The ability of manganese catalysts to activate $H_2O_2$ to oxidize various azo and phenolic dyes in aqueous carbonate buffers was studied by Eldik and co-workers.[10] The formation of a Mn(II) -$HCO_3$ complex was proposed on the basis of UV/Vis absorption spectroscopy and electrochemistry. Precipitation of $Mn(II)CO_3$ was observed in the absence of substrates, while addition of the azo and polyphenolic dyes inhibited the precipitation through complexation. The formation of the catalytically inactive species ($Mn(IV)O_2$) upon reaction of Mn(II) with $H_2O_2$ in $NaHCO_3$(aq) was confirmed by UV/Vis absorption spectroscopy and ESR.[11] Kinetic analysis was interpreted as indicating that peroxycarbonate, a more reactive oxidant than $H_2O_2$, formed in situ and presented the rate-limiting step in the reaction.[12] Comparison of the catalytic activity of Mn(II) salts with $[Mn(II)(bpy)_2Cl_2]$ and $[Mn(III)Mn(IV)(\mu\text{-}O)_2(bpy)_4](ClO_4)_3 \cdot 2H_2O$ in the bleaching of dyes indicated common reactive intermediates.

In this chapter the focus is on understanding the behavior of complexes such as **1** during catalytic oxidations under conditions relevant to modern industrial bleaching. The activity of the catalytic system (i.e. **1**) in the oxidation of styrene sulfonate, a conjugated olefin with high solubility in aqueous media, is studied, due primarily to its lack of pH chemistry (Figure 1). The pH dependence of the structure of the complex present in water between pH 6 and 9; the rate of oxidation of styrene with **1** and with Mn(II) salts; and the role of sequestrants, such as DTPA, that are used industrially, on the reaction rate and efficiency were studied with UV/Vis absorption and Raman spectroscopy. The study of the reactivity of Mn(II) under the same conditions was carried out to exclude or implicate the species it forms, in the chemistry observed with **1**; i.e. is **1** a catalyst or simply a source of Mn(II). Here, the major part is focused on control experiments with Mn(II) salts and the effect of variation in the amount of carbonate.

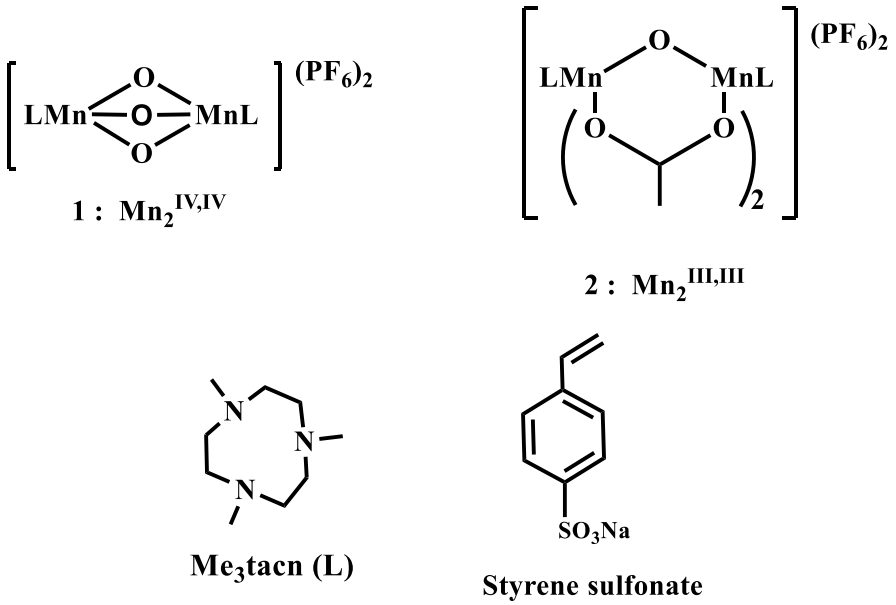
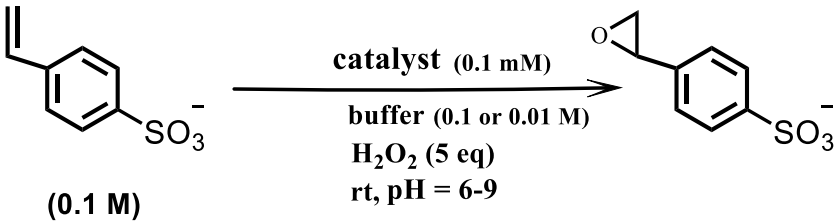



**Figure 1 Structure of complexes 1 and 2, the ligand tmtacn and substrates styrene sulfonate (SS)**

## 5.2 Results

### Reaction monitoring by UV/Vis absorption, Raman and resonance Raman spectroscopy

Scheme 1 shows typical reaction conditions applied in the present study. The activity of **1** and Mn(II) ions was investigated and compared in the absence and presence of bicarbonate, acetate and borate (common reagents employed in industrial bleaching processes). Raman spectroscopy was used to monitor changes in the concentration of styrene sulfonate and its epoxide product. The bands in the range 1600–1650 $cm^{-1}$ are characteristic of C=C stretching vibrations of vinyl and aryl groups and in particular the band at 1630 $cm^{-1}$ is useful in monitoring reaction progress.[13]




Scheme 1 Catalysed oxidation of styrene sulfonate (SS) with $H_2O_2$.

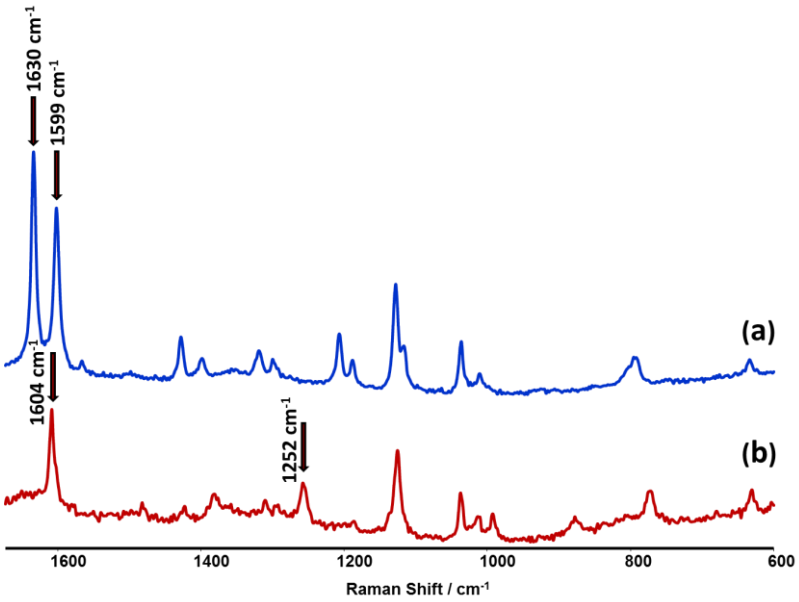



Figure 2 Raman spectra ($\lambda_{exc}$ 785 nm) of (a) SS and (b) the epoxide product OSS

The UV/Vis absorption spectra of **1**, $H_2O_2$ and 0.1 M carbonate buffer (w.r.t. water) are shown in Figure 3. Despite the complete absorption of light by $H_2O_2$ in the UV region, the visible absorption bands of **1** enable monitoring of its concentration and changes to the complex over time, e.g., by monitoring absorbance at 315 nm.

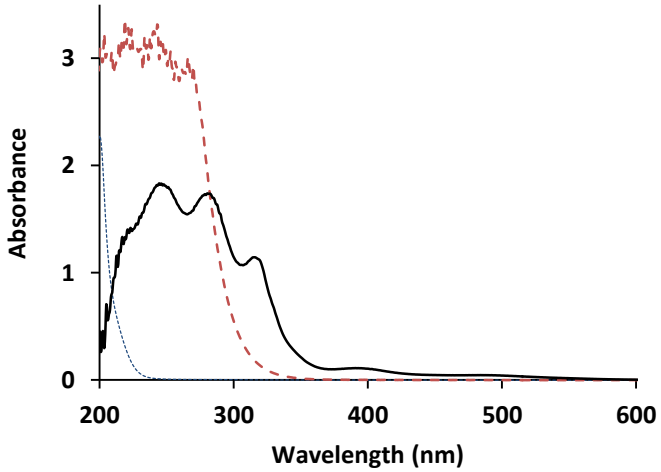



Figure 3 UV/Vis absorption spectra of 1 (0.1 mM, thick line), $H_2O_2$ (0.5 M, dashed line) and bicarbonate (0.1 M, dotted line) with respect to water as reference.

### Stability of 1 in carbonate buffer in the presence of $H_2O_2$

The effect of the bicarbonate/carbonate on the structure of **1** was monitored by Raman spectroscopy ($\lambda_{exc}$ 355 nm, Figure 4) over 23 h after the addition of $H_2O_2$. The spectrum after 23 h shows the complete consumption of the $H_2O_2$ (876 $cm^{-1}$) without significant disturbance of the Mn(μ-$O_3$)Mn core of **1** (699 $cm^{-1}$).

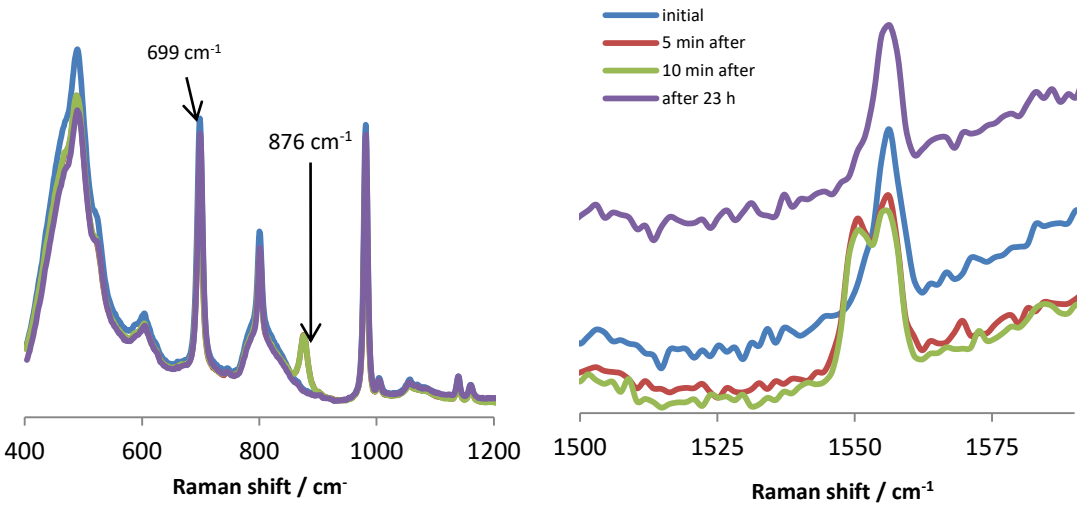



Figure 4 Raman spectra ($\lambda_{exc}$ 355 nm) of a solution of $H_2O_2$ (0.5 M), and 1 (3 mM) in $NaHCO_3$ (aq. 0.1 M, pH 8.6) (left) and increase in dissolved $O_2$ (1550 $cm^{-1}$) (right). Spectra acquired before (blue), and 5 min (red), 10 min (green) and 23 h (purple) after the addition of $H_2O_2$.

It is apparent that in $NaHCO_3$(aq), $H_2O_2$ has no noticeable effect on **1** manifested in the constancy of the Raman band of **1** at 699 $cm^{-1}$ and absorption spectrum[9,14] but that $H_2O_2$ decomposition proceeds quickly through disproportionation to water and $O_2$ (1550 $cm^{-1}$).

### Dependence of the rate of oxidation of styrene sulfonate on the concentration of 1 and of Mn(II)$SO_4$

The rate of epoxidation of styrene sulfonate and the disproportionation of $H_2O_2$ in $NaHCO_3$(aq) (0.4 M, pH 8.6) was determined with **1** over the concentration range 50 – 200 μM and with Mn(II)$SO_4$ between 0 – 200 μM (Figure 5). The rate of epoxidation of styrene sulfonate shows a linear dependence on the concentration of **1**, however, the rate of disproportion of $H_2O_2$, shows no dependence. Notably, however, the duration of the lag period before which $H_2O_2$ disproportionation commenced was inversely dependent on the concentration of **1**. In contrast to **1**, with Mn(II)($SO_4$) both the rate of epoxidation of styrene sulfonate as well as the disproportion of $H_2O_2$ depend logarithmically on concentration.

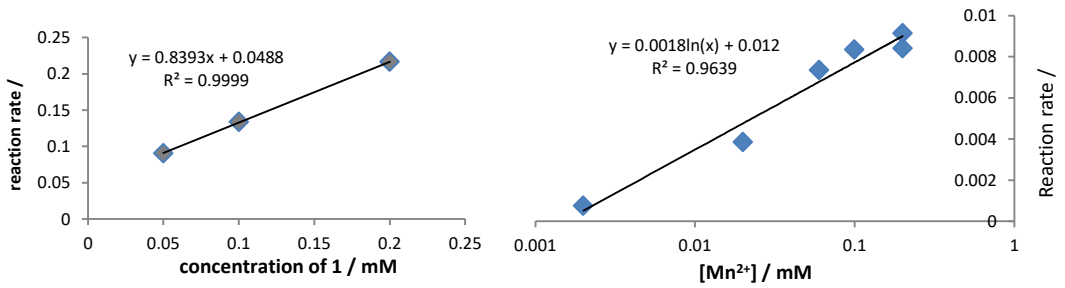



Figure 5 Dependence of the rate of the oxidation of the styrene sulfonate (right) on 1 and (left) on Mn(II)($SO_4$).

The logarithmic trend in both the rate of disproportionation and styrene sulfonate oxidation indicates that the actual concentration of 'available' manganese ions in the presence of carbonate is limited both by solubility and by the rate of formation of insoluble manganese oxides – indeed examination of the Pourbaix plot for manganese indicates that Mn(II) is not stable at pH 8.6. Indeed in the absence of styrene sulfonate a dark precipitate formed rapidly upon addition of $H_2O_2$ to a bicarbonate buffered solution of Mn(II)$SO_4$. The Raman spectrum of the precipitate (Figure 6) obtained after the reaction of Mn(II) ions with $H_2O_2$ in the absence or presence of substrate show differences when compared to the spectrum of $MnCO_3$, in particular the bands at ~580 $cm^{-1}$ and ~630 $cm^{-1}$, which are characteristic of Mn oxides. [15,16]

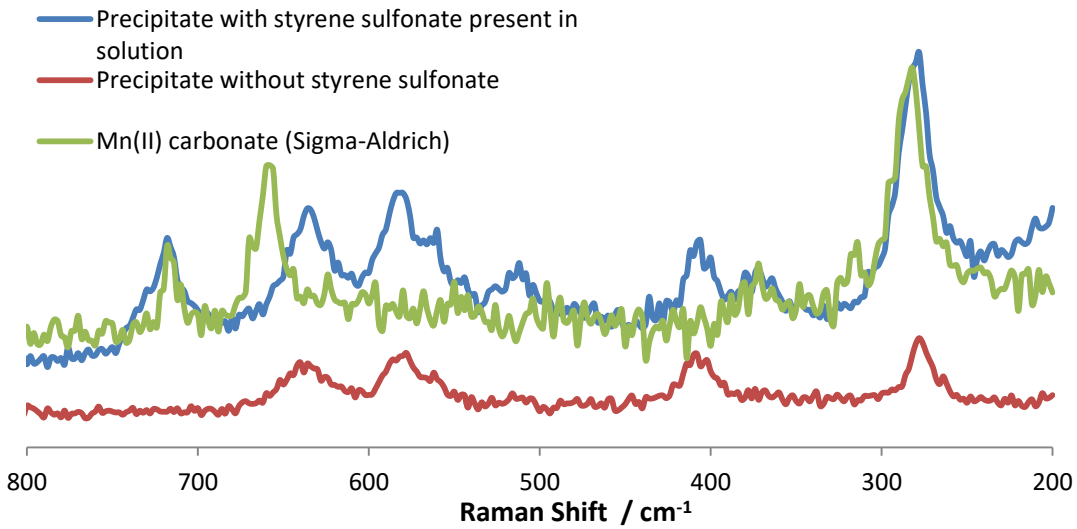



**Figure 6 Raman spectrum of $MnCO_3$ (green line) and the spectrum of the precipitate obtained after addition of $H_2O_2$ to the solution containing $MnSO_4$ (0.2 mM) and $NaHCO_3$ (0.1 M) (red line) and with SS (blue line).**

## Cooperative effects between 1 and Mn(II)

The oxidation of styrene sulfonate and the disproportionation of $H_2O_2$ in presence of both **1** and Mn(II) was considered, since **1** could be acting simply as a 'slow leak' source of Mn(II). The reaction was carried out with continuous variation of **1** and Mn(II)$SO_4$, with a constant concentration of 0.2 mM in manganese. Remarkably the effect of variation on both the rate of $H_2O_2$ disproportionation and styrene sulfonate oxidation is negligible, which indicates that under these conditions, the same catalytically active species (i.e. not **1** or its derivatives) is responsible primarily.

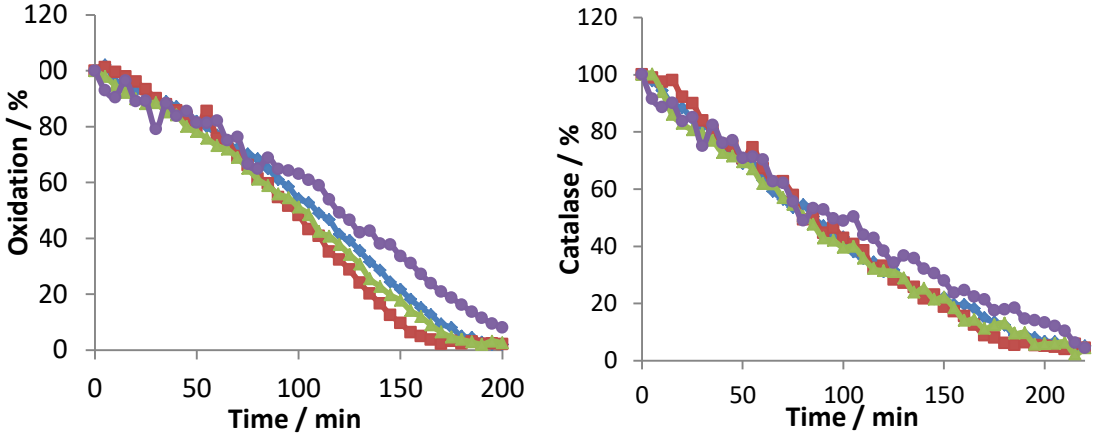



**Figure 7 Oxidation of styrene sulfonate with $H_2O_2$ in the presence of various mole ratios of 1 and Mn(II)($SO_4$). Monitor by Raman spectroscopy at $\lambda_{exc}$ 785 nm. Left: % styrene sulfonate remaining and Right: %$H_2O_2$ remaining. Reaction conditions: sodium sulfate (0.5 M) as internal reference, $H_2O_2$ (0.5 M), $NaHCO_3$ (0.1 M), styrene sulfonate (0.1 M), and $MnSO_4$ and 1 in ratios (Mn(II) / (Mn(IV) + Mn(II))): 0 (blue diamonds); 0.5 (red squares); 0.3 (green triangles); 1 (purple circles).**

### Effect of DTPA on the catalytic oxidation of styrene sulfonate with 1 or Mn(II)$SO_4$

A frequently used approach to eliminate the effect of adventitious metal ions in aqueous reactions is to add a sequestrant, which by virtue of its multidenticity prevents the metal ion from engaging in catalysis. Hence, the activity of Mn(II)$SO_4$ is expected to be eliminated upon addition of the sequestrant DTPA (Penta(carboxymethyl)diethylenetriamine). The effect of DTPA on the oxidation of styrene sulfonate with $H_2O_2$ in the presence of **1** was determined with in situ reaction monitoring by Raman spectroscopy. With Mn(II)$SO_4$, conversion was not observed in the presence of DTPA, while with **1**, activity was observed albeit with the addition of a lag phase that affected the oxidation of styrene sulfonate more so than $H_2O_2$. These data indicate that although DTPA inhibits the reaction catalysed by Mn(II)$SO_4$, it has a lesser effect on the activity of **1**. An experiment that raises a question mark over this conclusion is illustrated Figure 9.

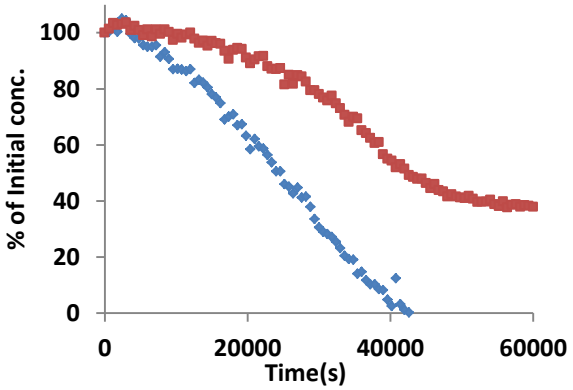



**Figure 8 Change in concentration of $H_2O_2$ (0.5 M) and styrene sulfonate (0.1 M), in $NaHCO_3$ (aq., 0.4 M, pH 8.6), with 1 (0.1 mM), and DTPA (0.1 mM). Conversion was determined from the normalised intensity of Raman bands due to $H_2O_2$ (876 $cm^{-1}$, blue diamond's) and styrene sulfonate (1633 $cm^{-1}$, red squares).**

Comparison of the reaction progress without DTPA present with an equivalent reaction in which DTPA is added after 50% conversion (Figure 9), shows that, even with **1**, DTPA does in fact stop conversion. Notably, however, after a considerable period of time, conversion continues again

with a rate similar to that observed without DTPA. These data indicated that a sudden change occurred in the reaction conditions.

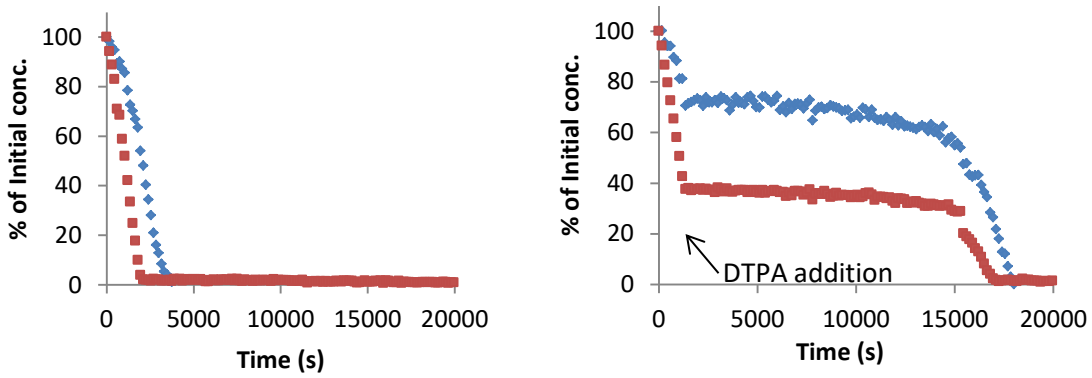



**Figure 9 Oxidation of styrene sulfonate (0.1 M) with $H_2O_2$ (0.5 M) catalysed by 1, and $Na_2SO_4$ (0.5 M) at pH 8.6 (0.2 M $NaHCO_3$). Styrene sulfonate (1633 $cm^{-1}$, red squares) and $H_2O_2$ (876 $cm^{-1}$, blue diamonds) were monitored by Raman spectroscopy. (left) Without DTPA, and (right) with DTPA (0.1 mM) added after 1350 s.**

Addition of $H_2O_2$ to a solution of **1** in 0.1 M $NaHCO_3$(aq) has no effect on the latter's absorption spectrum between pH 6 and 9 even over several hours in the absence of substrate. Furthermore, there is no evidence for significant decomposition of $H_2O_2$ over this period. The UV/Vis absorption spectrum of the reaction mixture (i.e. the absorbance of **1**) does not change significantly over the entire course of the reaction under standard conditions also (Figure 10). Reaction of **1** with $H_2O_2$ in the presence of 1 eq. of DTPA, however, shows a pH dependent lag phase after which a large change in the UV/Vis absorption spectrum is observed indicative of conversion of **1** to another species (Figure 10). A reasonable interpretation of the data is that an autocatalytic reaction leading to decomposition of the DTPA occurs rapidly at the end of the lag period, which 'unlocks' the reaction to Mn(II) salts formed by reduction of **1**.

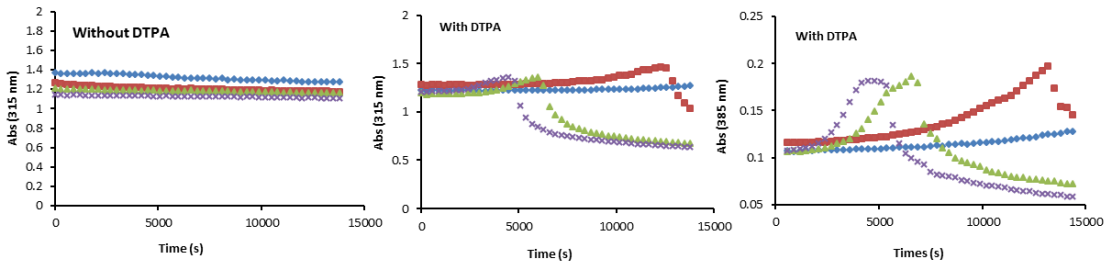



**Figure 10 pH dependence of the change in absorbance of the reaction mixture (without styrene sulfonate) at 315 nm with 0.5 M $H_2O_2$, 0.1 M bicarbonate, 0.1 mM 1 (left) and with 0.1 mM DTPA also (centre and right). pH 8.9 (purple crosses), 8.0 (green triangles), 7.2 (red squares), 6.1 (blue diamonds).**

### Effect of buffering agents on the reaction rate

The rate of epoxidation of styrene sulfonate in the presence of borate, acetate, water and bicarbonate was determined by reaction monitoring with Raman spectroscopy ($\lambda_{ex}$ 785 nm). As described above conversion under standard conditions is rapid in 0.1 M $NaHCO_3$(aq), whereas conversion is substantially slower without buffer or with acetate buffer and in borate buffer

conversion is not observed (Figure 11). These data raise the question whether carbonate is essential to the reactivity observed or if the other buffers inhibit the reactivity.

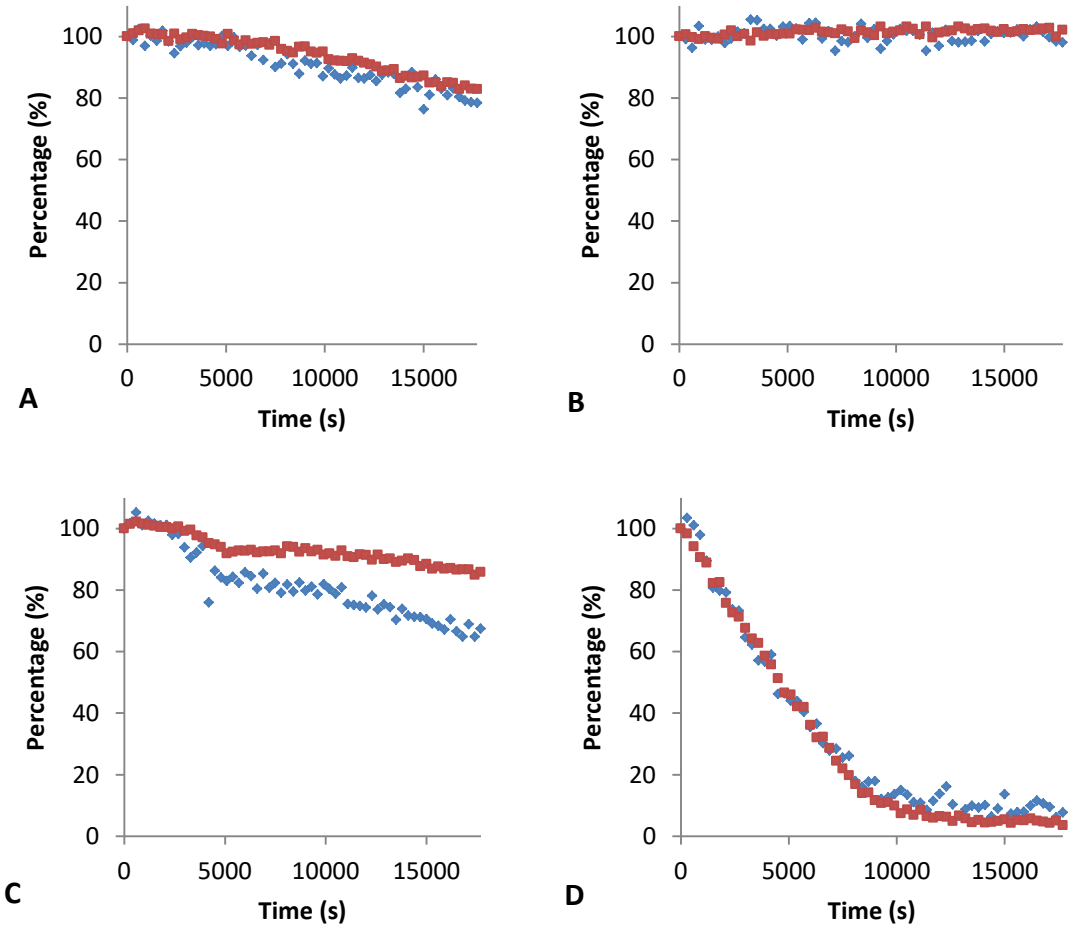



**Figure 11 Time dependence of conversion of $H_2O_2$ (0.5 M blue diamonds) and styrene sulfonate (0.1 M, red squares) with 1 (0.1 mM) and $Na_2SO_4$ (0.5 M, internal reference) at pH = 8.6 and (a) no buffer, (b) sodium borate (0.1 M), (b) NaOAc (0.1 M), and (b) $NaHCO_3$ (0.1 M).**

The effect of acetate and borate in the presence of bicarbonate, on conversion of both styrene sulfonate and $H_2O_2$ reveals that the presence of acetate has negligible effect in comparison to the reaction with carbonate alone (Figure 12), while the presence of borate increases the lag phase's duration and reduces the reaction rate substantially (Figure 13). Notably, however, a reduction in both the concentration of carbonate and borate results in a substantial decrease in reaction rate. These data indicate that carbonate is not acting simply as a buffer in the reaction but is actively involved, e.g., as a ligand etc.

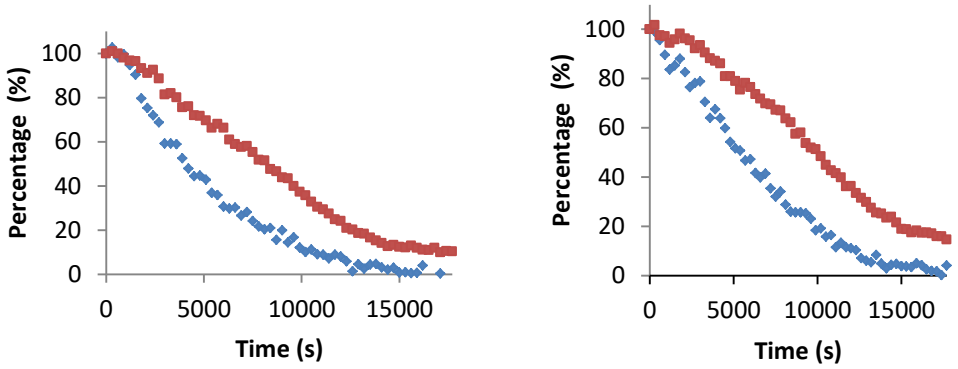



Figure 12 Time dependence of conversion of $H_2O_2$ (0.5 M blue diamonds) and styrene sulfonate (0.1 M, red squares) with 1 (0.1 mM) and $Na_2SO_4$ (0.5 M, internal reference) and $NaHCO_3$ (0.1 M, pH = 8.6), without (left) and with (right) NaOAc (0.1 M).

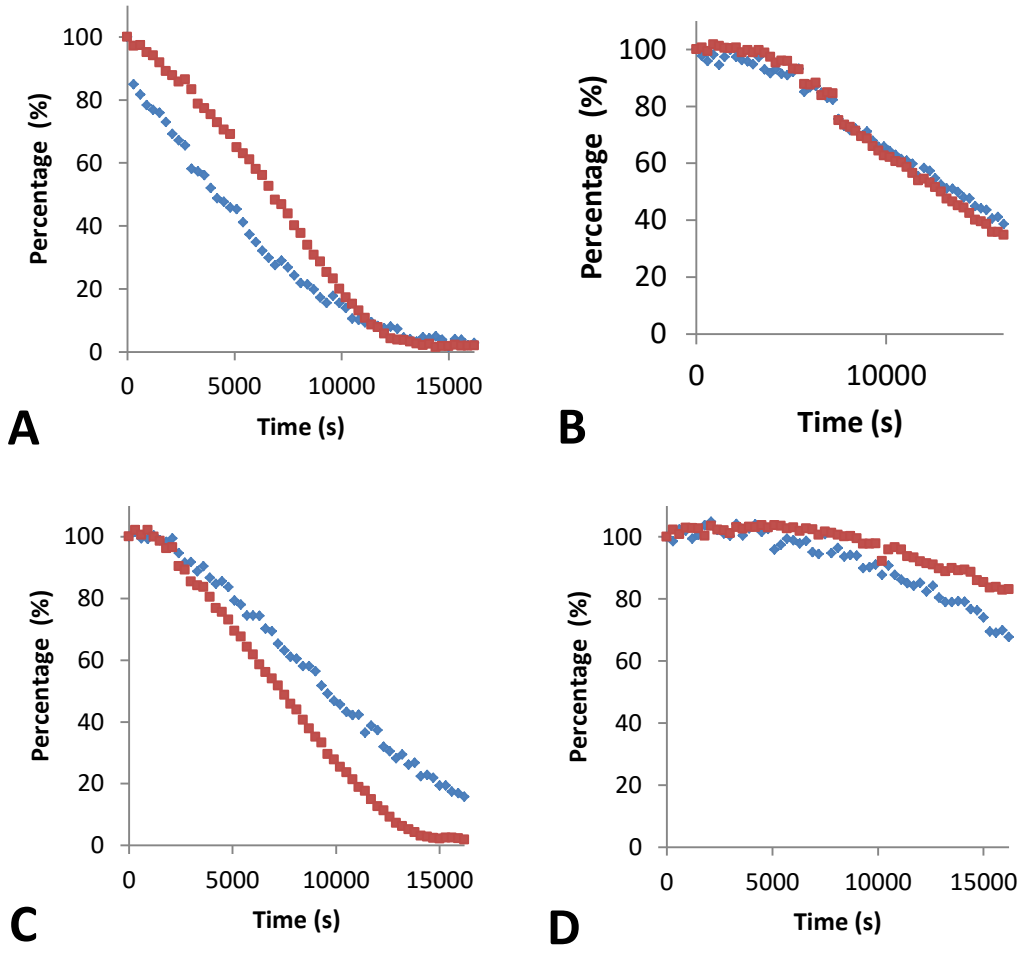



Figure 13 Time dependence of conversion of $H_2O_2$ (0.5 M blue diamonds) and styrene sulfonate (0.1 M, red squares) with 1 (0.1 mM) and $Na_2SO_4$ (0.5 M, internal reference) and $NaHCO_3$ (A-C 0.1 M, D 0.05 M, pH = 8.6), without (A) and with sodium borate (B 0.1 M, C &D 0.05 M).

As the borate buffer reveals a lag phase, a jump experiment was performed by adding borate (to 0.1 M) to a 0.1 M $NaHCO_3$(aq) solution after approx. 20% conversion of the substrate (Figure 14a). A control experiment in which 0.1 M $NaHCO_3$(aq) bicarbonate was added had no such effect (Figure 14b). In figure below, a drop in intensity is seen, which is observed as a drop in

concentration; however, this drop is assigned to absorption of the borate at different wavelengths.

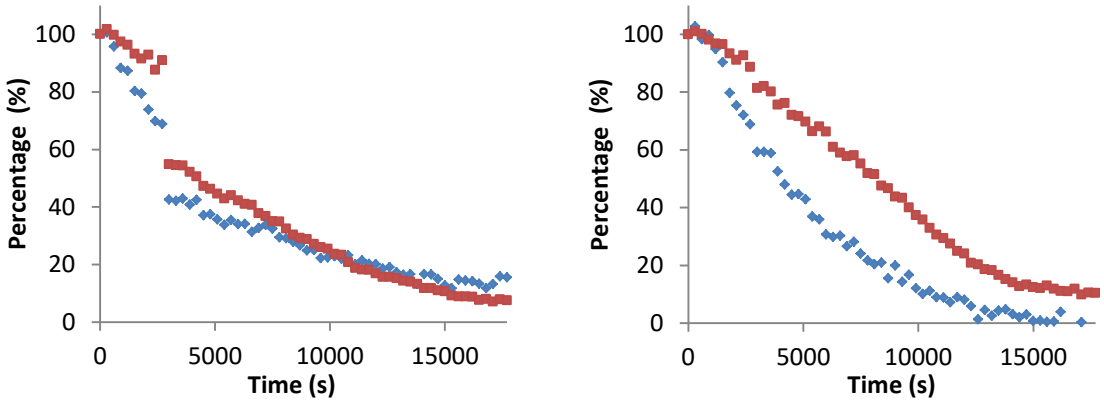



**Figure 14 Time dependence of conversion of $H_2O_2$ (0.5 M blue diamonds) and styrene sulfonate (0.1 M, red squares) with 1 (0.1 mM) and $Na_2SO_4$ (0.5 M, internal reference) and $NaHCO_3$ (0.1 M), (left) borate (0.1 M) was added after 2700 s and (right) the same volume of buffer containing 0.1 M $NaHCO_3$ was added after 2700 s.**

### In situ formation of percarbonate.

The formation of percarbonate has been proposed by several groups to rationalise the activity of Mn(II) salts in the epoxidation of alkenes and in the bleaching of model dyes.[17,18,10] A similar reaction could be expected in the case of borate buffer (i.e. the formation of perborate). The presence of such species under catalytic conditions was explored in an effort to understand the role of the buffering agents in catalytic oxidation of styrene sulfonate. The formation of perborate in solution is plausible, however, it is relatively insoluble in basic water and hence the effect of such a reaction would be to inhibit oxidation by removal of oxidant from the solution (vide supra).

It is conceivable that peroxido-compounds form from the reaction of $H_2O_2$ with $CO_2$, $HCO_3^-$, $CO_3^{2-}$. Raman spectroscopy 532 nm and 785 nm, however, does not provide evidence for the formation of percarbonate in solution. Comparison of the Raman spectra of a solution of commercial sodium percarbonate and of sodium bicarbonate with $H_2O_2$ (pH 8.5, Figure 15) reveals that the only difference between the solutions is in regard to the bands at 984 and 1070 $cm^{-1}$, which are due to differences in pH and hence the concentration of $CO_3^{2-}$ and $HCO_3^-$. However, the band at 984 $cm^{-1}$ does not correspond to any of the bands in the spectra of bicarbonate solution collected at pH between 12 and 7 (Figure 16).

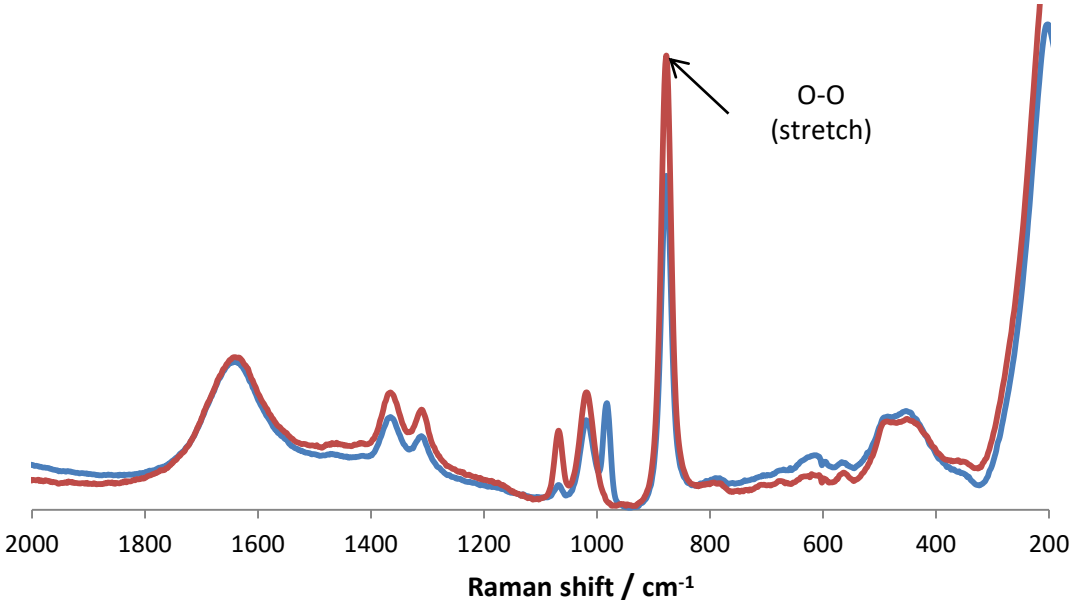



Figure 15 Comparison of Raman ($\lambda_{exc}$ 532 nm) spectra of a 500 mM solution (pH 8.3) of sodium percarbonate (blue line) and of a solution of sodium bicarbonate (500 mM) and $H_2O_2$ (600 mM) (pH 8.7, red line).

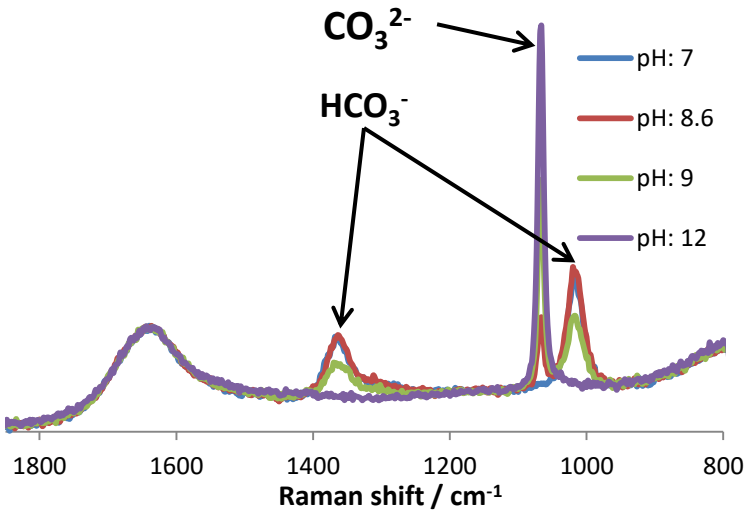



Figure 16 pH dependence of Raman ($\lambda_{exc}$ 785 nm) spectrum of a $NaHCO_3$ (0.5 M) aqueous solution.

### Catalytic activity of 1 under industrially relevant conditions:

Reaction progress monitoring of oxidation of the styrene sulfonate (SS) with $H_2O_2$ and **1** or Mn(II) was studied between pH 6 – 9 with a concentration of bicarbonate that is much less (10 mM) compared to studies described above and of more relevance to industrial conditions. In presence of Mn(II), conversion of styrene sulfonate was not observed over the pH range examined.

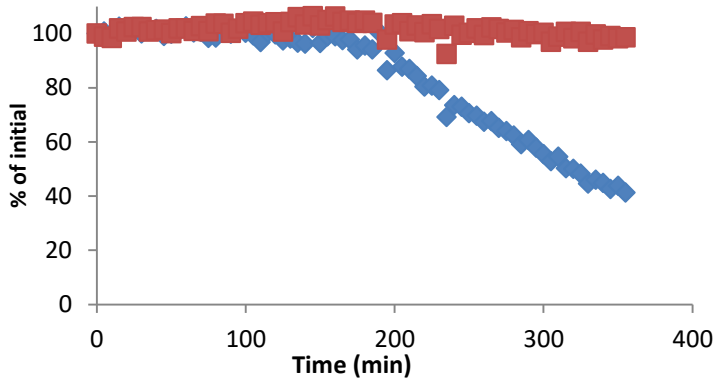



Figure 17 Time dependence of conversion of $H_2O_2$ (0.5 M blue diamonds) and styrene sulfonate (0.1 M, red squares) with Mn(II)$SO_4$ (0.2 mM) and $Na_2SO_4$ (0.5 M, internal reference) and $NaHCO_3$ (0.01 M, pH 8).

In contrast to **1**, although the reaction proceeds more slowly, conversion is observed. At pH 9 the lag phase decreases. Notably, although the rate of oxidation of styrene sulfonate shows little, if any, pH dependence, the rate of disproportionation of $H_2O_2$ increases with pH. (Figure 18)

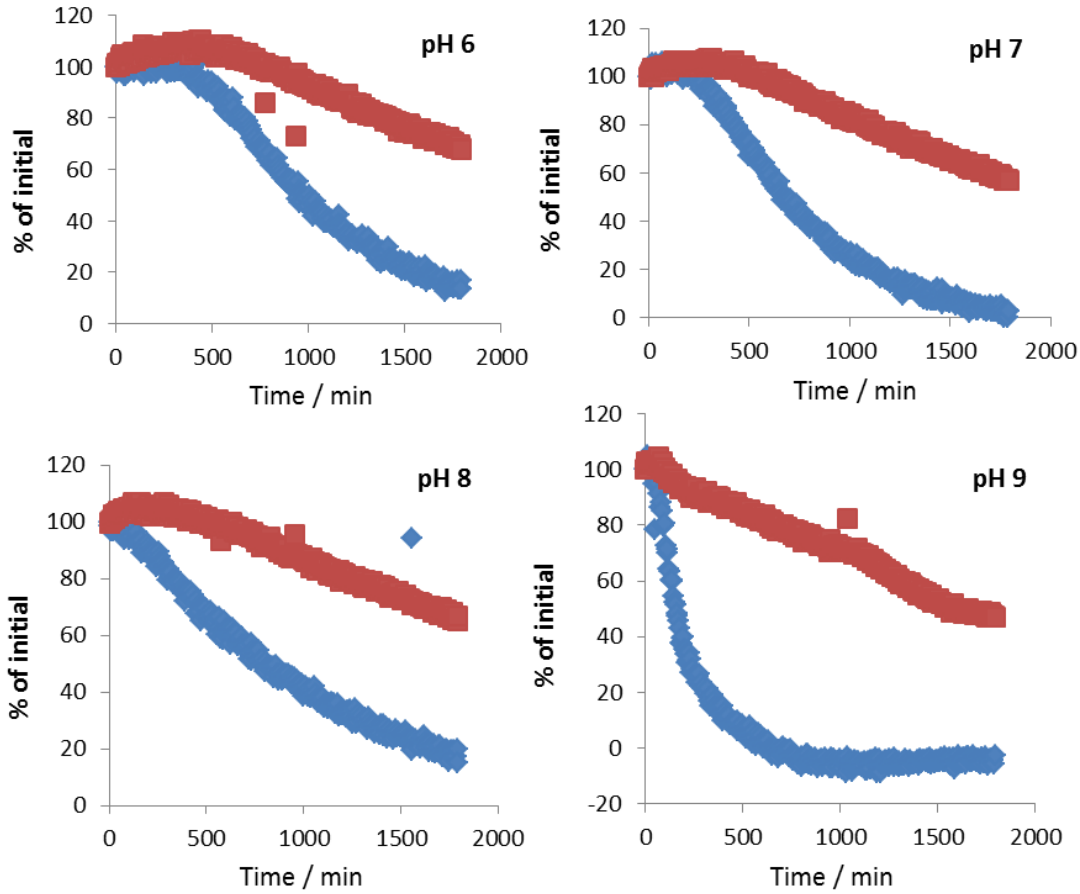



Figure 18 Time dependence of conversion of $H_2O_2$ (0.5 M blue diamonds) and styrene sulfonate (0.1 M, red squares) with 1 (0.1 mM) and $Na_2SO_4$ (0.5 M, internal reference) and $NaHCO_3$ (0.01 M). Upper left – pH 6, Upper right - pH 7; Lower left - pH 8; Lower right - pH 9.

## 5.3 Discussion

A key observation as to the physical changes that occur during the reactions is that the appearance of a brown precipitate is noticeably faster with Mn(II)$SO_4$ in the absence of substrate. This indicates that the formation of manganese oxides, which is thermodynamically favored at the pH of the solutions, is a slow process requiring nucleation. The dependence of the reaction rate on $\log_{10}$[Mn(II)] is consistent with the metastable situation that is encountered in the reaction; i.e. the manganese present should be in the form of manganese oxides but the formation of these is retarded by the presence of the substrate and accelerated due to the autocatalytic nature of their formation. Given that higher oxidation states are required to form the manganese oxides, the substrate can suppress nucleation by keeping the concentration of these species low. It is not inconceivable that the concentration of carbonate has a substantial influence on these processes given the low solubility of Mn(II)$CO_3$ ($K_{sp}$ 2.24 x $10^{-11}$). Hence, the actual steady state concentration of Mn(II) under reaction conditions is likely to be much lower than the analytical concentration. The effect of carbonate, although it is attractive to ascribe it to the formation of percarbonates, is therefore most likely due to its control on the steady state concentration of Mn(II). At lower concentrations of carbonate, its ability to inhibit the formation of manganese oxides is reduced non-linearly. Hence, the availability of catalytically active Mn(II) ions is drastically reduced and the disproportionation of $H_2O_2$ by the oxides at high pH is observed.

If it is presumed that Mn(II) ions are responsible for the catalysis observed and accepted that they are only present at low concentrations, then it is possible that the primary involvement of **1** in the reaction is to provide for a slow 'leach' of Mn(II) ions into solution.

A further argument in favor of the active catalytic species at high carbonate concentrations as being Mn(II) ions is provided by the effect of DTPA. DTPA sequesters metal ions effectively and suppresses the activity of Mn(II)$SO_4$ completely. In the case of **1**, DTPA does not halt conversion indefinitely, however reaction monitoring by UV/Vis absorption spectroscopy indicates that after a lag time the DTPA (which contains oxidizable amines) undergoes oxidative degradation, thereby releasing and Mn(II) ions captured.

At lower concentrations, where the activity of Mn(II) ions is negligible, then the conversion of substrate can be attributed to species derived from **1**. The lower reaction rates observed indicate that it may well show the same activity at higher carbonate concentrations but this would be masked by the activity of the Mn(II) ion based catalyst.

## 5.4 Conclusions

The reactivity of Mn(II) and **1** towards the oxidation of alkenes in aqueous solution is similar but not identical. Mn(II) presents a greater dependence on its own concentration and that of bicarbonate as well, whereas **1** shows a linear dependence of concentration on activity and depends less strongly on the presence of bicarbonate. It is remarkable that, in contrast oxidation in acetonitrile, in water **1** is unaffected by the presence of $H_2O_2$ (in absence of substrate at least). The difference in the requirement for carbonate/bicarbonate in solution points towards the possible formation of percarbonate species in the case of Mn(II) catalysed reactions, however, definitive evidence for its formation is elusive. The presence of borate, inhibits catalysis and

implies the in situ formation of the oxidant sodium perborate, however, while this species has not been observed it is clear that borate removes $H_2O_2$ by precipitation.

The most striking, and in many ways problematic, experiment is that with DTPA, which highlights how the presence of the sequestrant can prevent oxidation with Mn(II) but does not appear to affect the activity of **1** substantially. However, it is clear from the time dependent spectroscopy that in fact DTPA undergoes oxidation and therefore releases the bound ions into solution. These data raise the question whether or not **1** is acting as a Mn(II) reservoir and provides for a jumping off point for further studies of this complex system.

## 5.5 Experimental

### Materials

Styrene sulfonate (Sigma Aldrich) and $H_2O_2$ 50 % aqueous solution (Acros) and all the other commercially available chemicals were used without further purification unless stated otherwise. $[Mn(IV,IV)_2(\mu\text{-}O)_3(tmtacn)_2](PF_6)_2$ (**1**) was available from earlier studies.[9]

### Instrumentation

Raman spectra were recorded using a Perkin-Elmer Raman Flex equipped with a fibre-optic probe ($\lambda_{exc}$ 785 nm) at room temperature, typically with 10 exposures of 8 s duration. Raman spectra ($\lambda_{exc}$ 355 nm) were recorded as described in chapter 4. UV/vis absorption spectra were recorded with a HP8453 spectrophotometer or a Specord600 (AnalytikJena) in 1 cm path length quartz cuvettes.

### Catalysed oxidations

Oxidation of styrene sulfonate was carried out in a cuvette (3 mL total volume) according to the following protocol: Double distilled water was used to prepare a stock solution of 0.5 M $Na_2SO_4$, from which a buffer solution (typically 0.1 M) was prepared. A stock solution containing the **1** or $MnSO_4$ (3 and 6 mM, respectively) was prepared in parallel. The reaction mixture was prepared directly in the cuvette by addition of the appropriate volumes of buffer, the catalyst and, at the start of the experiment, aq. $H_2O_2$ with vigorous mixing. Typical concentrations employed were 0.1 M substrate, 0.1 mM catalyst and 0.5 M $H_2O_2$. Time zero is taken to be the point at which the catalyst is added. The epoxide, product of SS, was isolated and characterized by $^1H$ NMR spectroscopy as described elsewhere.[13]

### Analysis of Raman spectra

Raman spectra were analysed in the spectral range 1800 to 600 $cm^{-1}$. The data analysis used the area of the bands between 1600 and 1650 $cm^{-1}$, which includes contributions from the reactant and products only. The band at 870 $cm^{-1}$ was used to determine $H_2O_2$ concentrations. **1** and **2** were monitored at $\lambda_{exc}$ 355 nm in the range 400 to 1000 $cm^{-1}$.

## 5.6 References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